SCIENCE FOR GLASS PRODUCTION

UDC 666.11;546.2666.1-911.48

STRUCTURE OF SOL-GEL SILICA VITRIFIED UNDER PRESSURE

O. A. Ivanova,[1] G. T. Petrovskii,[1] A. D. Semenov,[1] A. N. Smirnov,[1]
V. E. Ter-Nersesyants,[1] V. S. Shashkin,[1] and A. E. Chmel'[1]

Based on the results of the study, monolithic blocks of vitreous SiO_2 were obtained by reaction vacuum-compression sintering (RVCS) of silica-bearing sol-gel products. The conditions of the synthesis, the parameters and mechanisms of the processes, and the properties of the obtained material are described.

The traditional methods of sol-gel synthesis have disadvantages that do not depend on the kind of initial products, i.e., long-term gel dehydration in the stages of drying, calcination and sintering and limited sizes of the specimen obtained. Sintering can be activated by using high pressure [1], but compression solves the problem of fabricating vitreous SiO_2 (c-SiO_2) at a relatively low temperature only partially if the reaction of dehydration is not activated. In the present work we established that control over the removal of chemically bound water makes it possible to synthesize c-SiO_2 at a temperature not exceeding 1200°C.

We used powdered silica of grades OSCh 7-4, OSCh 12-4 and OSCh 11-4 synthesized by hydrolysis of tetraethoxysilane and xerogels obtained from silica sols of grades K1 and OSCh 6 – 3. For comparison, we tested the initial material consisting of milled quartz glass of grade KU with an initial content of OH-groups not exceeding 140 mln⁻¹.

The powdered silica was characterized by high purity and homogeneity (the amount of impurities was 10^{-4} wt.%); the content of alkali cations that markedly affect crystallization processes did not exceed 5×10^{-3} wt.%. The calcination temperature of the first two materials was at most 800°C, that of the latter material (OSCh 11-4) was 1200 – 1300°C. The OSCh 11-4 material had the lowest water content of all the silicas (2000 mln⁻¹ in accordance with the specification).

Silica gels K1 and OSCh 6 – 3 had the form of colloidal solutions of silica with a density of 1.02 – 1.04 g/cm³ and pH ~ 8.5; the mass fraction of solid phase was 21 – 25%. The silica sols differed greatly in the size of the particles. In monodisperse K1 silica sol, the diameter of particles of the predominant fraction was about 10 nm. The proportion of the coarse disperse fraction with particles over 60 nm in size was

less than 0.5%. In polydisperse OSCh 6-3 silica sol, the size of the particles was 7 – 13 times larger than in the K1 sol.

The powdered silicas were milled in a Pulverizette ball mill in an agate drum with agate balls for 25 min to a coarseness of < 20 μm. The gels obtained from sols K1 and OSCh 6-3 were transformed into xerogels by heat treatment (heating to 800°C) with holding for 30 min at the final temperature. The powders were compacted at the specified sintering temperature in a vacuum furnace with a graphite heater. The motion of the punch that transferred the force of the press to the specimen placed in the vacuum furnace was controlled with a micrometer. The value of the specific deformation δ (%) was calculated by the formula

$$d = 100 l_i l_\tau^{-1},$$

where l_i and l_τ are the lengths of the specimen in the compaction process and due to total deformation in time τ, respectively.
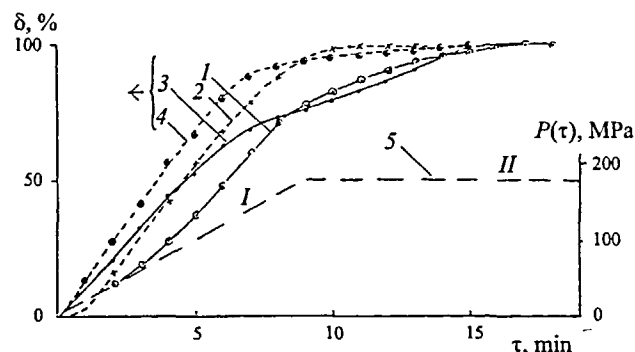

Fig. 1. Diagram of RVCS. *1, 3, 2, 4*) Dependences δ(τ) at 1150 and 1200°C, respectively; *5*) algorithm of application of pressure p (τ); initial material: *1, 2*) SiO_2 OSCh 7-4; *3, 4*) SiO_2 OSCh 12-4.

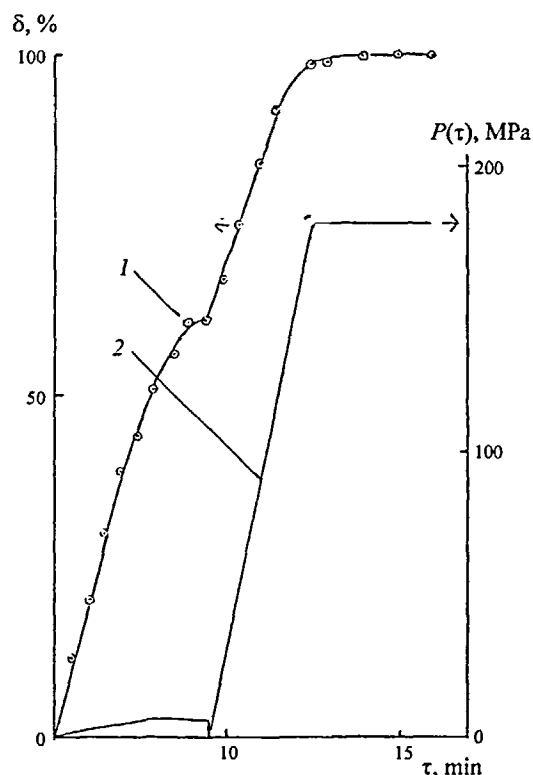[1] GOI S. I. Vavilov GP VNTs.

Fig. 2. Dependence $\delta(\tau)$ for a SiO_2 specimen of grade OSCh 7-4 in the process of two-stage RVCS molding. *1*) Deformation at 1150°C; *2*) algorithm of application of pressure.

Fig. 3. Dependence of the content of retained OH groups in vitreous specimens on the sintering temperature.

Figure 1 presents a sintering diagram. At a relatively low pressure (region *I* of curve *5*), deformation of all specimens occurs quite actively and δ attains 75 – 95%. In the final stage of deformation at a constant pressure (region *II* of curve *5*), the dependence $\delta(\tau)$ asymptotically approaches $\delta = 100\%$, which indicates that the specimen has attained the maximum density. The density of specimens sintered under these conditions amounts to 2.206 ± 0.004 g/cm^3. It is obvious that the difference in the deformation at the studied temperatures is caused by differences in the kinetics of dehydration of the material of the specimens, the degree of ordering of the spatial structure of the glass-forming skeleton, and the presence of viscous flow. First, the rate of the dehydration process changes with an increase in the temperature; second, the process of removal of physically and chemically sorbed water is superimposed on the process of dehydration of OH groups that causes formation of SiO – Si bonds due to polycondensation. At 1200°C the process of structure formation begins to be influenced by viscous flow.

The sintering regimes used correspond to optimum conditions of plastic deformation. In the case of the use of xerogels synthesized from silica sols, these conditions are determined first by the kinetics of deformation of the initial materials (Fig. 2). In the process of two-stage pressing of one specimen, the dependence $\delta(\tau)$ was measured between inter-
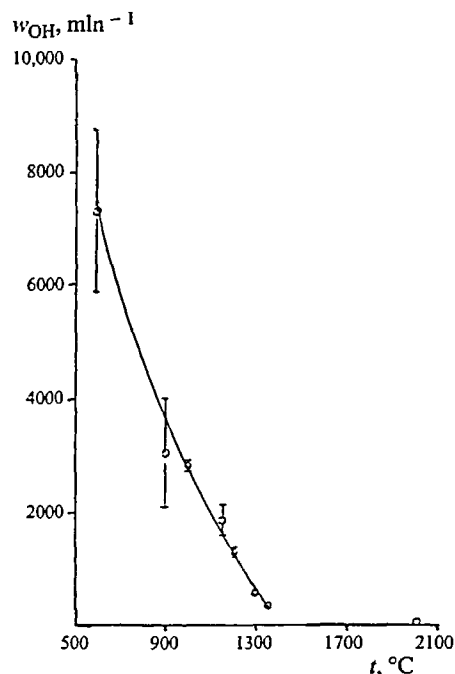
mediate exposure an uncompacted specimen in air, as a result of which the structure of the xerogel bonds disturbed in the first pressing stage, including the OH groups, was considerably restored. In the second stage of reaction vacuum-compression sintering (RVCS), the dependence $\delta(\tau)$ repeated the form of the first stage. Therefore, it was very important to control the dehydration process and the content of water in the initial materials.

The content of OH groups in the intermediate vitreous materials and the obtained quartz glass was determined by different methods. Rutherford back scattering was used when the content of OH groups exceeded 3000 mln^{-1}. The method of detecting recoil protons was used to determine the absolute content of hydrogen in the standard glass whose absorption spectrum was used to compare to the infrared absorption spectra of specimens of quartz glass where the content of OH groups was below 3000 mln^{-1}. In order to measure the content of OH groups by the method of infrared absorption we used three absorption bands, i.e., the fundamental absorption peak at $\lambda = 2.7$ μm and its two harmonics at $\lambda = 1.38$ and 2.21 μm. The extinction coefficients for these bands were chosen in accordance with [2, 3].

Table 1 presents the averaged measured contents of OH groups in vitreous products obtained under a pressure of 150 – 170 MPa from various initial raw materials. The results of measurements of the content of retained OH groups in the vitreous products obtained by traditional sol-gel synthesis on the basis of silica sols and from Aerosil dispersions of grade OKh50 produced by Degussa (Germany) with pre-

liminary electrophoretic deposition of the powders are given for comparison.

It follows from Table 1 that the kind of initial raw material, if not prepared specially, has little effect on the content of retained OH groups. The data for specimens based on OSCh 11-4 silica sol are not presented in Table 1 because the specimens did not transmit light, though it could be expected that the content of OH groups in them should be minimum. We used the data in Table 1 for plotting the dependence of the content of retained OH groups in vitreous sol-gel materials on the sintering temperature (Fig. 3). To make the behavior of the curve more descriptive we used the value of 46 mln^{-1} obtained for standard KI quartz glass (treated at 2000°C) as the extreme point. In the 1000 – 1350°C range, removal of chemically bound water was intense and the content of OH groups diminished by an order of magnitude. The mean temperature in the region of the linear drop was 1175°C. The sintering diagrams presented in Figs. 1 and 2 show that the requisite density of the quartz glass is attained at treatment temperatures of 1150 – 1200°C.

Table 2 presents the content of OH groups in specimens of quartz glass fabricated by the method of RVCS from raw material with a different prehistory (preliminary calcination). It can be seen that preliminary calcination of the raw material reduces the content of retained OH groups in any molding regime. The effect of calcination is highest when it is conducted at 800°C and followed by molding at 1200°C.

It is known [4] that the total amount of steam emitted in heating powdered specimens of SiO_2 OSCh 7-4 and SiO_2 OSCh 12-4 to 1150°C is equal to 4 and 37 vol.%, respectively. This is connected first with the high initial content of water in the raw OSCh 12-4. As a result, the retained content of OH groups in specimens fabricated from this material is higher. Glass specimens obtained from SiO_2 OSCh 6-3 sol have less OH groups, which can be associated with the more uniform distribution of single SiO_2 particles and the corresponding decrease in the concentration of aggregates. It seems quite obvious that by increasing the RVCS temperature of the powdered specimens from 1150 to 1200°C, we should reduce markedly the content of OH groups (to ≤ 100 mln^{-1}).

In testing the preliminary preparation of the powder to be molded that consisted of xerogel based on SiO_2 OSCh 6-3 silica sol, we subjected it to screening of the fraction less than 20 μm in size, elutriati-

on, and calcination at 800°C and obtained quartz glass specimens with a stable content of OH groups at the level of ≤ 50 mln^{-1}. A similar result was obtained for a model specimen from milled KU1 quartz glass with screening of the fraction less than 20 μm in size (the initial content of OH groups was about 140 mln^{-1}, the final one was below 50 mln^{-1}). This corresponds approximately to the content of OH groups in standard quartz glasses of grade KI (< 40 mln^{-1}).

The structure of the formed material was controlled by methods of infrared reflection spectroscopy and Raman spectroscopy (RS) of light to optimize the conditions of its synthesis. The temperature conditions of the sintering process corresponded to the final stage of transformation of the xerogel into glass, which was characterized by total collapse of the pores (Fig. 4) and structural relaxation of the material. Since the temperature conditions of drying (calcination) of the raw material did not envisage heating above 800°C, the internal structure of the material should change intensely in formation of the monolith. It could be expected that the sintering process would be highly sensitive to the parameters of the process regime and hence its optimization would require a certain effort. Changes occurred both in the parts fab-

TABLE 1

Heat treatment temperature, °C	Content of retained OH groups in the specimens, mln^{-1}			
	RVCS product from SiO_2 OSCh 12-4	RVCS product from SiO_2 OSCh 7-4	Sol-gel product, synthesis without filler	Product of electrophoretic deposition
600	7300 ± 1400	–	–	–
900	3050 ± 950	–	–	–
980	–	–	2800 ± 100	–
1150	2450 ± 90	1590 ± 60	–	–
1200	1170 ± 120	1150 ± 210	1430 ± 120	–
1300	–	–	–	572 ± 21
1350	–	–	–	353 ± 13

TABLE 2

Temperature of calcination of the raw material, °C	Content of OH groups, mln^{-1}, in specimens of quartz glass*					
	OSCh 7-4 (1150°C)	SiO_2 OSCh (1200°C)	OSCh 12-4 (1150°C)	SiO_2 OSCh (1200°C)	SiO_2 sol (1150°C)	OSCh 6-3 (1200°C)
600	–	–	–	840 ± 90	–	–
700	–	–	–	770 ± 30	–	–
800	1460 ± 150	272 ± 17	–	750 ± 30	1090 ± 40	≤ 100
900	–	1030 ± 130	–	1070 ± 40	–	–
1000	–	–	–	308 ± 11	–	–
1100	–	–	–	1063 ± 40	–	–

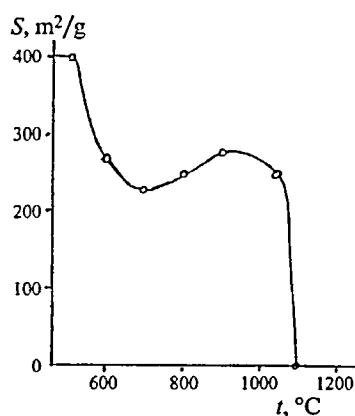* The temperature of the RVCS is given in parentheses.

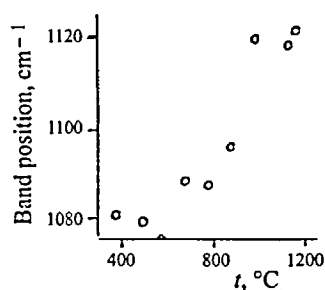**Fig. 4.** Dependence of the effective surface area S of xerogel on the temperature t of the heat treatment.

Fig. 5. Dependence of the frequency shift of the 1100-cm^{-1} band on the heat treatment temperature of xerogels.

Fig. 6. Raman scattering spectrum in the region of the boson peak: 1) for a treatment temperature of 900°C; 2) 1000°C; 3) SiO_2 melted in air.

ricated by the method of RVCS and in the batches of gel glass having the form of polished plates that served as model specimens.

The infrared spectrum of the reflection from the glass bears information on the chemical structure of the specimen. The spectrum of c-SiO_2 has a dominant band in the region of 1100 cm^{-1} (oxygen vibrations in $Si-O-Si$ groups [5]) whose precise position depends on the mean value of the SiOSi valence angle in the material. The x-ray data show [5] that the most equilibrium (energetically favorable) configuration is characterized by an angle of 144°, which corresponds to the position of the mentioned band in the IR reflection spectrum at a frequency of 1122 cm^{-1}. The change in
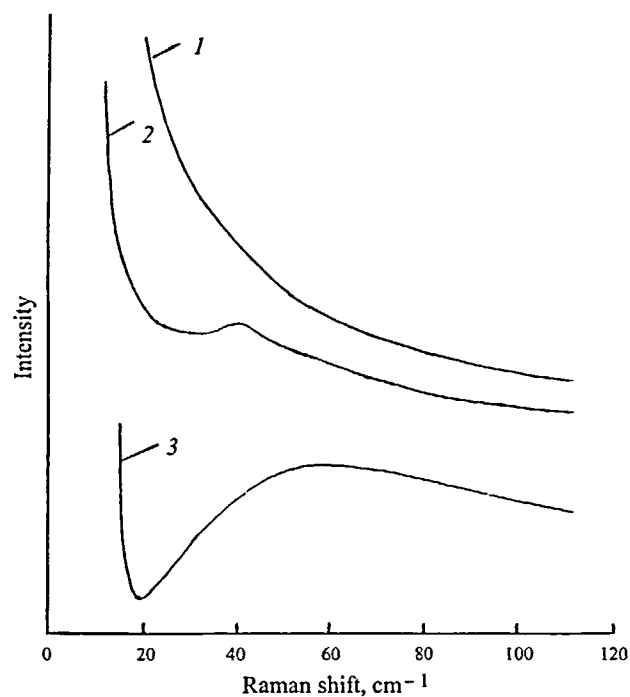
TABLE 3

Parameter	Method of manufacturing c-SiO_2			
	Melting in air	Melting in H_2	Chemical precipitation from vapor	RVCS
Frequency shift of the 1100-cm^{-1} band, cm^{-1}	2.0	3.0	2.0	0.0
Correlation radius, nm	0.44	0.44	0.44	0.53

this position of the band (if it occurs) is a sign of a certain imperfection of the structure; such a frequency shift of the band is observed in specimens fabricated by various methods (Table 3).

Figure 5 presents the temperature dependence of the precise position of the 1100-cm^{-1} band. The position of the band changes gradually from 1080 to 1095 cm^{-1} as the calcination temperature is increased from 300 to 900°C and "jumps" to 1119 cm^{-1} at a temperature of 1000°C. Further growth of the heat treatment temperature affects the position of the band inconsiderably. Consequently, at 1000°C the internal stresses (nonequilibrium deformations) that appear at lower treatment temperatures, for example, in the process of random coalescence of gel particles, relax [6]. When recording the spectrum of a specimen sintered at 1200°C we established that the band has a frequency of 1122 cm^{-1}, i.e., corresponds to the most relaxed chemical structure.

In the region of the RS spectrum (below 100 cm^{-1}), the glasses exhibit a band not connected with the specific chemical structure. It is known as the boson peak, whose position characterizes the size of the correlation sphere, i.e., a certain statistical ordering of the structure of an amorphous substance [7]. It is shown in [8, 9] that the "intermediate-range order" responsible for the boson peak is absent in "green" gels and appears only in the late stages of heat treatment. In other words, if the RS spectrum of the material contains a boson peak, it can be inferred that the gel-to-glass transformation was finished on the structural level. We used this fact

for determining the temperature range in which the green product can be transformed into a vitreous state and for establishing the physicochemical state of the sintered material.

In the study of the xerogels, we established the appearance of boson peak in the RS spectrum after annealing the model specimens at $900-1000°C$. This temperature range coincides with the region where the IR reflection spectrum exhibits relaxation of atomic deformations of the vitreous skeleton. The frequency of the boson peak v_B in the RS spectrum differs considerably from the frequency typical of molten SiO_2, i.e., $45-52$ cm^{-1} versus 60 cm^{-1}, respectively (Fig. 6). This result indicates a difference in the correlation radii R of the materials, because it is known [8] that $v_B \cong v/R$ (where v is the speed of sound).

We calculated that the radius of the correlation sphere in the sintered xerogels exceeded that in vitreous SiO_2 obtained by other methods (see Table 3); the considerable growth of the correlation sphere is a sign of substantial ordering of the spatial structure. In this respect the data from RS spectroscopy agree with the results of the study of the IR spectra and show that the vitreous skeleton in the sintered material has a highly equilibrium configuration. In other words, on the submicroscopic level, the obtained monolithic SiO_2 is more perfect than vitreous SiO_2 of other origins. This result is important for estimating the efficiency of the process of sintering of powdered gel silica.

The successful fabrication of monolithic blocks of vitreous SiO_2 by reaction vacuum-compression sintering of sol-gel products is determined to a considerable degree by the possibility of controlling the process of dehydration of the material both in the stage of preparing the raw materials and in molding. The production cost can be diminished by establishing the conditions that would ensure the minimum temperature of the final process. The regime determined in

the present work allowed us to fabricate monolithic preforms at a temperature not exceeding 1200°C. A spectroscopic study conducted for controlling the fullness of transformation of the gel product into vitreous material proves the efficiency of the determined conditions for preparing and sintering gel powders into preforms suitable for the optical industry.

REFERENCES

1. M. Decottignies, J. Phalippou, and J. Zarzyki, "Synthesis of glasses by hot-pressing of gels," *Mat. Sci.*, 13, 2605–2618 (1978).
2. O. Humbach, H. Fabia, U. Grzesik, et al., "Analysis of OH absorption in synthetic silica," *Non.-Cryst. Solids*, 203(1), 19–26 (1996).
3. K. M. Davis, A. Agarwal, M. Tomozawa, and K. Hirao, "Quantitative infrared measurement of hydroxyl R. F. concentration in silica glass," *Non.-Cryst. Solids*, 203(1), 27–36 (1996).
4. V. N. Rodicheva, A. A. Koryavin, V. S. Shashkin, et al., "A study in the field of physical chemistry and technology of glass and pyrocerams," *Trudy Inst. GIS*, 13–19 (1981).
5. B. E. Warren and R. L. Mozzi, "X-ray diffraction in vitreous SiO_2," *Appl. Cryst.*, 2(1), 164–168 (1962).
6. A. Chmel, E. K. Mazurina, and V. S. Shashkin, "Vibrational spectra and defect structure of silica prepared by non-organic sol-gel process," *Non.-Cryst. Solids*, 122, 185–290 (1990).
7. V. K. Malinovskii and A. P. Sokolov, "The nature of boson peak in Raman scattering of glasses," *Solid State Comm.*, 57, 757–761 (1986).
8. M. G. Murtagh, E. K. Graham, and C. G. Pantano, "Elastic moduli of silica gels prepared with tetraethoxysilane," *Am. Ceram. Soc.*, 69(11), 775–779 (1986).
9. J. I. Rousset, E. Duval, A. Boukenter, et al., "Gel to glass transformation of silica," *Non.-Cryst. Solids*, 107(1), 27–34 (1988).